



New measurements and analysis of the far-infrared spectrum of CH₂DOH in the lowest torsional vibrational state (e_0)



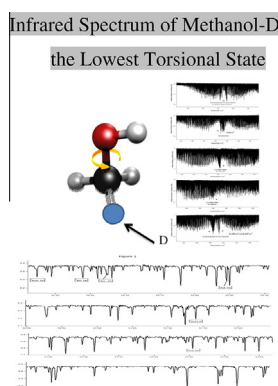
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HIGHLIGHTS

- New lower temperature spectra have been used to determine the transition wavenumbers more precisely.
- New Q-branches have been identified to provide additional confirmation.
- Assignments are confirmed by combination loops in situ using Q and R branch lines.
- The results will be useful for Astronomical and laser discovery.
- Corroborate MMW spectral study.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work the far infrared (FIR) absorption spectrum has been measured for the asymmetrically mono deuterated Methanol (CH₂DOH) species in the wavenumber range of 15–1200 cm⁻¹ better accuracy and signal/noise ratio than known before. Assignments have been made for b-type transitions in the lowest lying torsional vibrational state trans-(e_0) for a wide range of rotational angular momentum. The assignments have been rigorously confirmed by the residual loop defect methods. The 'R-branch wavenumbers are analyzed by the usual state dependent expansion parameters and the Q-Branch origins. These origins have been used to calculate the torsional and torsional-rotation interaction contributions. These findings are in good agreement with predicted from the Hamiltonian model described in recent publications. A large number of assignments have also been made in the millimeter wave spectrum recorded earlier and thereby evaluated the asymmetry splitting parameters for 4 different axial rotational angular momentum quantum numbers. The analysis and interpretation of the spectra are reported. New assignments for about 260 transitions are included the text and a catalog of about 1500 transitions belonging to the e_0 species is prepared (Appendix 1) and is made available through the open server in "Research Gate" and will be freely available to others.

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1. Introduction

The asymmetrically mono deuterated methanol (CH₂DOH) exhibits complex spectra in the far infrared (FIR) and millimeter

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wave (MMW) regions of the electromagnetic spectrum. The understanding of the inner details of the energy level pattern possesses a challenge to spectroscopists. This molecular species is also a source of strong FIR laser lines optically pumped by the CO₂ laser operating in the 10 μm region [1–5]. This molecule is also quite abundant in interstellar space [6,7]. The presence of this

species may prove important to determine the Deuterium/Hydrogen ratio which may throw some light into the early stages of the baby universe and to unlock the chemistry in the region where they are discovered. Normally astronomers' favorite place into look at is the star forming regions which are copious source of infrared emission.

High resolution spectroscopy has been used extensively in other in order to aid these studies. In a recent publication the need for such as the present work was discussed [8]. It was discussed that there need to be more reliable information with improved accuracy. Keeping these in mind it was decided to record the whole spectrum at a lower temperature using "Fourier Transform" (FT) spectrometer at the maximum allowed resolution. The acquisition of the entire spectra with best possible conditions using a "Synchrotron Radiation" source is underway at the Canadian Light Source in Saskatchewan.

In the present work the spectra recorded at $-60\text{ }^{\circ}\text{C}$ not only increase the S/N ratio but also enhances the population of lower lying states and reduces noise in the spectra. The spectra originating from higher lying states also become less intense because of the reduction of the Boltzmann factor for these states. This provides a cleaner spectrum and instead of finding peaks by a routine commercially available peak finding routine the spectral maxima have been directly observed using the IGOR program. This made any overlapping lines or broad features are disentangled better because judgement can be made by direct observation. Under these conditions the commercial peak finding routine can provide dubious numbers. The improved resolution and signal to noise (S/N) ratio allowed not only correcting some assignments in the literature but also providing new Q-branch assignments and providing the valuable loop residual technique to defiantly confirm the assignments. Lower temperature operation of the sample also enables the reduction of the width of the spectral lines due to Doppler broadening hence providing more accurate peaks. A direct look at the spectrum and the corresponding assignments guided more by physical reasoning than by mathematical computation comparison. As discussed before combination loops of closed lines which in confirmed assignments. In this communication, a catalog of about 1450 assigned spectral lines has been prepared and is being kept in an open source web server, whereas new assignments for about 260 R branch transitions are presented in Table 1 whereas the complete atlas of assigned transitions are gathered in Appendix-1 and will be made available freely from an open source web server. The results should be useful for "radio astronomers" and in the field of optically pumped FIR lasers.

2. Experimental

The FIR spectra have been recorded at a different run at a lower temperature ($-60\text{ }^{\circ}\text{C}$) and low pressure 0.1 mtorr at the Justus Liebig Universität in Germany. To eliminate the presence of water vapor the sample cell has been conditioned by heating and flashing out with Nitrogen gas. A small amount of CO_2 gas was introduced in the cell for calibration purposes. It should be noted that throughout this work only the low temperature spectra have been used. These spectral lines have better line shapes; more precision and physical discretion was used when encountering overlapping lines or localized perturbations. It should be noted that using only the technique of Q-branch lines and computational results (which complements each other) could lead to invalid rotational angular momentum quantum number assignments [9]. Not simply having the associated R/P branches could lead to problem because confirmation by the loop residual method can't be applied for confirmation of the assignments. All these have been avoided from the start of this work as far as possible. These have been discussed

in detail in our previous communication [8]. It should be noted that Pearson et al. [10] have studied the first three torsional vibrations states but their study mostly used MMW spectra. Some FIR Q-branch data from the same source as our previous work were used which had lower precision. In order to compare the lower temperature spectra comparisons are made between the present spectra and the room temperature spectra in the identical range in Figs. 1 and 2. From Fig. 1 it is clear that the present spectra look much cleaner with little noise. It should be noted that the feature around 72.19 cm^{-1} does not even appear in the present spectra. It is speculated to due to stray contaminants e.g. water vapor. Similar cleanliness and lower spectral width can clearly be noticed in the spectrum in the range of $61\text{--}62\text{ cm}^{-1}$. The advantage of the zooming facility in IGOR resulted in a precise determination of even very weak lines.

The MMW spectra were recorded using a backward wave oscillator based spectrometer employing the FASST (Fast Scan Sub-millimeter Spectroscopy Technique) at the Ohio state University at the laboratory. The FASST system is simple in concept and straightforward in execution. In this method a Backward Wave Oscillator (BWO) tube (ISTOK OB-30) is used to cover the 240–375 GHz region. Similar tubes are available for the 100–1000 GHz region [11]. The beam splitter (BS1) is used to split the output power of the BWO, with absorption cell of length 1–10 m and detected by an InSb hot electron bolometer. The remaining Fabry–Perot (FP) cavity via a mylar beam splitter, which provides fringes for frequency interpolation between reference spectral lines of known frequency. In order to maximize the dynamic range of the spectrum, the low frequency roll off in the analog amplifiers between the detector and the A/D input to the computer is adjusted to provide an approximately first derivative line shape and to generally suppress the recording of the power variations of the BWO and multi-path interference effects. For the study of weaker lines, additional analog gain is used at the expense of the measurement of the amplitude of the stronger lines. In the current system (which is not optimized for sensitivity), strongly absorbing lines are of S/N 10^4 in 1 MHz of bandwidth (1 ms of integration time). Comparison of spectra obtained on phase locked systems with FASST spectra shows that they too are Doppler limited. Here we will provide an overview and focus on those aspects most important for analytical systems: the characteristics of the BWO sub-millimeter source and the optical frequency calibration scheme. The spectra were recorded in a number of closely spaced ranges: 128–146, 150–170, 180–258, 260–360, 462–506, and 598–610 GHz for CH_2DOH and 111–161, 146–182, 193–213, 224–264, 261–325, and 328–365 GHz for CHD_2OH . The selection of these ranges seems random but it was decided by the BWO equipped with the spectrometer at the time when the instrument was available for the present measurements. A sample of the clean MMW spectra can be seen in Fig. 3. These two types of spectra (MMW and FTIR) complement each other and help to confirm the validity of the assignments using the close loop residual method. This method is independent of the Energy model used.

3. Interpretation and analysis

The presence of the off-axis deuterium in the methyl top in this molecule makes the molecule to depart from the C_{3v} symmetry group. This removes the degeneracy of the energy levels and makes them highly mixed and rendering torsional vibration quantum numbers not being a good quantum number resulting in relaxation of the selection rules than in other symmetric methanol species [11–14]. This makes the spectra many fold crowded compared to the symmetric parent species. In order to be able to identify the spectra we employed the Internal Axis Method (IAM) theory to

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